



Photodegradation of Insecticide Chlorpyrifos in Aqueous Solution under Simulated Solar Light Irradiation Conditions using Babolrood River Water

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Abstract

Chlorpyrifos is an organophosphate insecticide, used to control foliage and soil-borne insect pests on a variety of food and feed crops. In the natural environment, Chlorpyrifos can be degraded through several possible processes, including photodegradation, biodegradation, and hydrolysis. In the present work the photodegradation and environmental fate of Chlorpyrifos in aqueous phase under simulated natural conditions in the presence of artificial UV-light was investigated. The gas chromatography-mass spectrometry (GC-MS) identification of Chlorpyrifos photodegradation products suggested the formation of only one major product, i.e., Chlorpyrifos-oxon. Based on the structurally identified photoproduct a plausible degradation pathway is proposed for the photolysis of Chlorpyrifos in natural water over UV irradiated.

Keywords: Chlorpyrifos, Photodegradation, Simulated solar light irradiation, Organophosphorus compound.

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Introduction

In recent years, synthetic insecticides have been used *increasingly*, because of their widespread availability, simplicity in application, efficacy and economic returns besides having huge environmental costs. Insecticides are considered cumulative and toxic compounds. Their presence as contaminants in aquatic environments may cause serious problems to human beings and other organisms. Excessive and injudicious use of insecticide lead the environmental contamination in air, water, soil besides accumulating in food chain. Chlorpyrifos (IUPAC name: *O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate) (Figure 1) is a crystalline organophosphate insecticide and is commonly used to control insects on agricultural crops such as cotton, grain, fruit, alfalfa, and sugar beets. It acts on the nervous system of insects by inhibiting acetyl cholinesterase. Chlorpyrifos is moderately toxic to humans and chronic exposure has been linked to neurological effects, developmental disorders, and autoimmune disorders [1]. In the natural environment, Chlorpyrifos can be degraded through several possible processes, including photodegradation, biodegradation, and hydrolysis. Photodegradation is the most common degradation processes in the environment and has the advantage of having a higher degradation rate and being faster than biodegradation and hydrolysis. It is of great research significance and highlights the importance of understanding the processes, mechanisms, intermediates, and final products of the photodegradation of Chlorpyrifos within the natural environment. Since the formation of highly toxic reaction intermediates is possible, identification of the degradation products is essential. [2,3] The purpose of this study was to analyze and identification the photodegradation products of Chlorpyrifos using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Based on the identified intermediates, a plausible degradation pathway for Chlorpyrifos is proposed.

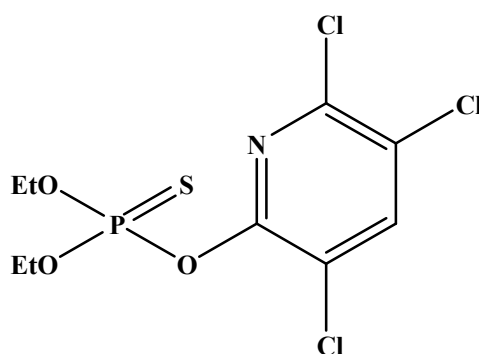


Figure 1. Structure formula of chlorpyrifos.

Experimental

Chemicals and Reagents

Chlorpyrifos technical grade (90.0%) was a gift from Iran Chemical Complex. Analytical grade standards of high purity were obtained from Fluka and were used without further purification and all the chemicals and solvents were obtained from E-Merck (Darmstadt, Germany).

Water sampling

Natural waters used in the experiments were collected from the Mazandaran province in North Iran and was natural water of Babolrood River. The natural water sample collected from the top meter of water body in 2.5-L pre-cleaned amber glass bottle and stored at 4°C prior to use. Water sample was used without previous treatment and filtration. Physicochemical characteristics of sample of Babolrood River natural water are given in Table 1.

Table 1. Physicochemical properties of the Babolrood River.

pH	Conductivity ($\mu\text{S/cm}$)	TDS ¹ (mg/L)	TOC ² (mg/L)	Salinity (‰)	NO ₃ ⁻ (mg/L)
7.52	401	221	2.85	0.41	3.43

¹TDS: Total Dissolved Solids, ²TOC: Total Organic Carbon

Photoreaction apparatus and procedure

For the photodegradation experiments the UV Chamber used was of rectangular in shape having dimensions of length 4.5 ft, width 3.0 ft and height 3.5 ft (Figure 2) and made up of GI sheet. It was equipped with seven 36 W UV tubes (Philips) attached to the roof having wavelength of 365 nm fitted in parallel on the top of the chamber. Small holes were drilled on the sidewall of the chamber to maintain a constant temperature and for proper circulation of air. The reactor (17 cm in diameter and 5.3 cm in height made up of borosil glass) was placed on a lab jack so that required intensity could be attained by adjusting the distance of the reactor from the UV tubes. The UV intensity in the reactor can be varied from 10 to 35 Wm⁻² corresponding to the average intensity of UV radiation in sunlight. The process was carried out in open atmosphere and oxygen purging was done from time to time. Temperature inside the reactor was maintained by an exhaust fan [4,5].

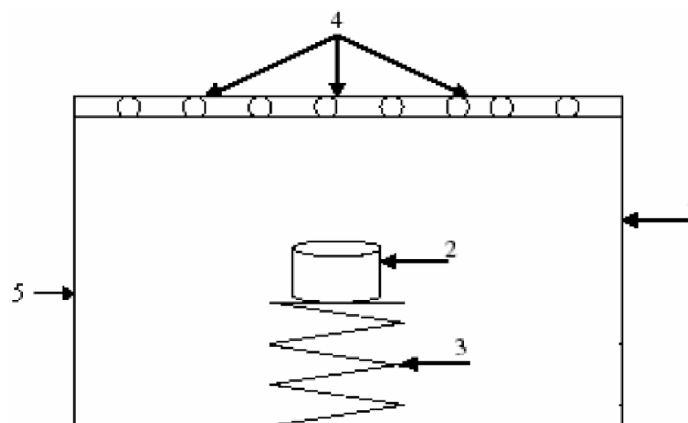


Figure 2. Schematic diagram of lab scale set up.

(1) UV chamber, (2) Reactor, (3) Lab jack, (4) UV lamps, (5) Holes

Irradiation experiments were carried out by exposing 200 ml of aqueous solution Chlorpyrifos (20 mg/L) containing 0.2% sodium azide (for biological degradation resistance) under artificial solar irradiation. During irradiation, the samples were magnetically stirred. All experiments were carried out at room temperature and pH 6. A dark control experiment was also conducted in this experiment. The treated water samples were processed for Chlorpyrifos photodegradation on one hour after treatment [6].

Extraction procedure

Treated water samples (200 ml) were taken in a separator funnel and 10 g sodium chloride was added. Photoreactions of Chlorpyrifos photodegradation in different solvents (such as n-hexane, methanol/water) were also studied. The photoproducts in the methanol/water solution were twice extracted by n-hexane. The n-hexane layers were then combined into a centrifuge tube. The extracted liquid was then evaporated to 1 mL under a stream of nitrogen for GC analysis. The final samples were stored in the dark place while awaiting analysis.

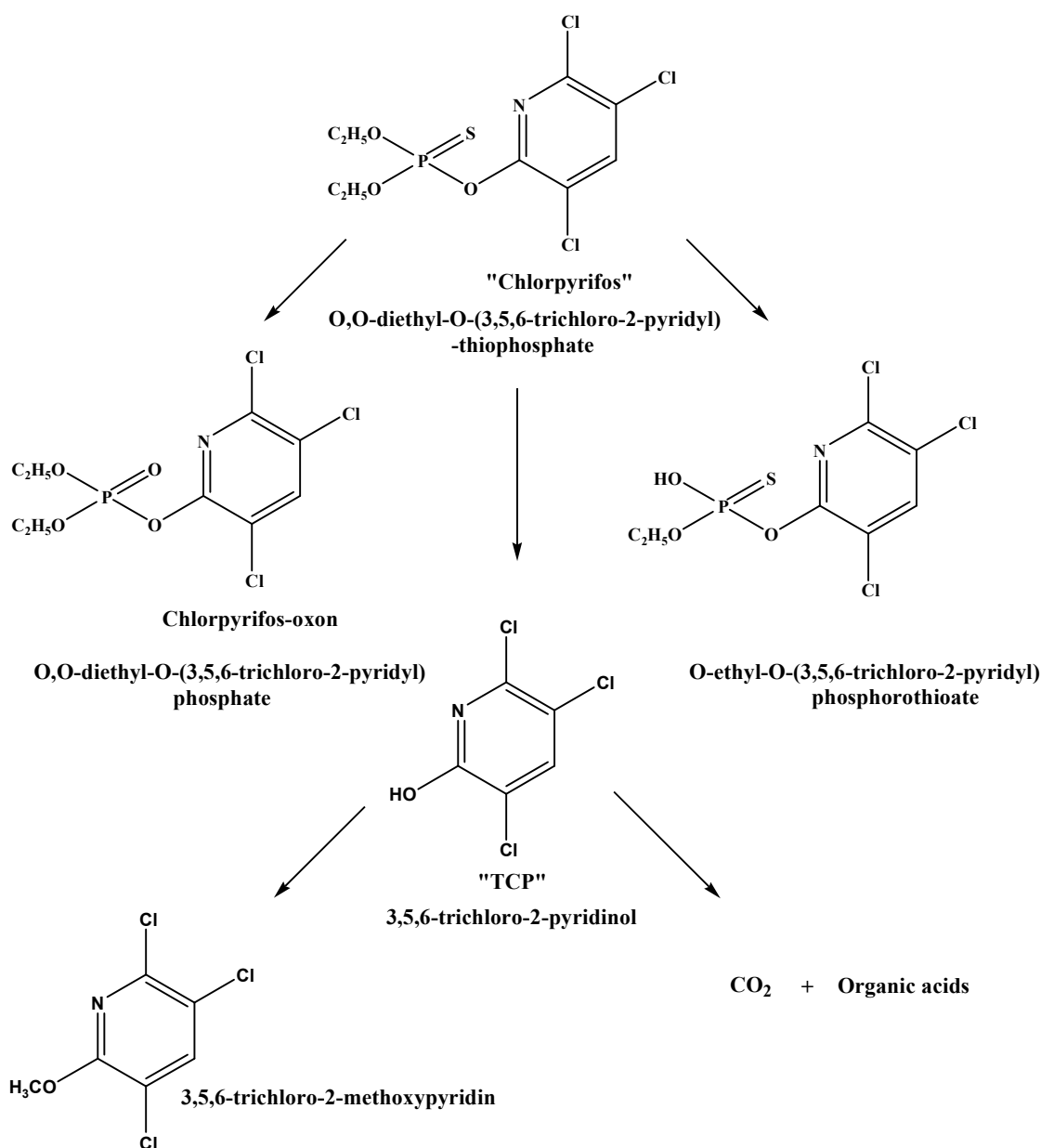
Analysis

All the samples were stirred for 2 minutes with 5 ml of hexane using a Vortex in order to extract the remaining compounds. After that, the samples were analyzed by GC/MS following Method 6410B of “Standard Methods” (American Public Health Association 2005). A Hewlett-Packard system consisting of a 5890 GC system equipped with a micro-electron capture detector (μ ECD) and A DB5-M column (30 \times 0.25 mm i.d.) was programmed from 60(1)- 4-300(15) and an Agilent 5975C mass spectrometer coupled to GC was used to analyze the photoproducts. Chromatographic data were monitored by Xcalibur[®] 1.4 software. Injector temperature was

250 °C, range mass 50–450 amu. The MS was operated in electron ionization mode with a potential of 70 eV. The spectra were obtained in full scan mode. Helium was used as the carrier gas [6,7].

Results and discussions

The photodegradation of Chlorpyrifos by simulated sunlight in water has been studied. Light is the one of the powerful agents of OP environmental degradation pathway [8,9]. The photolysis of OP can occur by direct photolysis, since they exhibit absorption max in UV region (240-310 nm). Photodegradation rates depend on a number of factors including the wavelength and intensity of light, the transparency of the medium, and the properties of the environment itself. The photodegradation of Chlorpyrifos may occur via two reaction patterns. It might be initiated by the cleavage of either an ethyl-group or a chloro-group resulting in the formation of [O-ethyl-O-(3,5,6-trichloro-2-pyridil)-hydrogene-phosphorothioate] and [O,O-diethyl-O-(3,5-dichloro-2-pyridil) phosphorothioate]. The following step of the decomposition is the scission of chloro and ethyl groups ([O-ethyl-O-(3,5-dichloro-2-pyridil)-hydrogene-phosphorothioate]). Breaking away of another chloro-group leads to the formation of [O-ethyl-O-(5-chloro-2-pyridil)-hydrogene-phosphorothioate]. Loss of the other ethyl-group transforms the previous compound into the end-product [O-(5-chloro-2-pyridil)-dihydrogene-phosphorothioate]. The GC-MS identification of Chlorpyrifos photodegradation products suggested the formation of only one major product. Compound identified according to mass spectra is Chlorpyrifos-oxon: 300 (37%), 298 (52%), 272 (48%), 270 (73%), 199 (71%), 197 (77%). No other products, such as diethyl phosphate ester or 3,5,6-trichloro-2-pyridinol as a result of bond cleavage were observed in the experiment. The lack of detection of 3,5,6-trichloro-2-pyridinol and observation of only one major product, lead us to additional efforts in search of the pathway of Chlorpyrifos transformation [10-12]. A generalized Chlorpyrifos degradation pathway which may occur in the environment has been postulated. Chlorpyrifos is thought to be hydrolyzed to TCP and subsequently converted to TMP and CO₂ as a primary degradative pathway (Scheme 1).



Scheme 1. Scheme of the proposed photodegradation pathway for chlorpyrifos.

Conclusions

The extensive use of pesticides, in order to enlarge the production in agriculture, has led to a growing accumulation of pollutants in the environment over the last decades. Organophosphorus (OP) pesticides are among the most widely spread pollutants used for insect control. They have replaced organochlorine compounds, since they are easily degraded and they are not accumulated in the environment for a long time. Information on degradation products is necessary to understand the environmental fate of pesticides and to establish important degradation pathway, which will allow us to get a better knowledge of the transformation of target compounds in the environment. Moreover, the study of contaminant photochemical behavior is a key issue in terms of the formation

of toxic transformation products. The photodegradation of Chlorpyrifos under simulated solar light irradiation conditions on natural water of a river in North of Iran has been studied. The results reported here show that the combination of gas chromatography-mass spectrometry analysis, positive and negative ions and exact mass measurements represent a powerful analytical approach for the confirmation of the molecular structure of photodegradation intermediates. More detailed research on the degradation mechanism of Chlorpyrifos, however, should be further explored.

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